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Collection Efficiency Evaluation of Mercury-Trapping Media for the SASS Train Impinger System

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COLLECTION EFFICIENCY EVALUATION OF MERCURY-TRAPPING MEDIA FOR THE SASS TRAIN IMPINGER SYSTEM

by

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16. ABSTRACT The report gives results of an investigation of the collection efficiencies of the popularly used media in the SASS train impinger assembly. A simple mercury-vapor generator system, based on saturation of air with mercury vapor at a fixed temperature, was assembled. Performance evaluation of the system indicates that stable atmospheres of mercury can be generated with the equilibration temperatures controlled by Graham condensers. By repeated sampling and analysis of the generated atmospheres and by calibration of an on-line atomic absorption spectrometer (AAS), the absorbance readings can be converted directly into mercury concentrations; i.e., micrograms per cubic meter. With stable and known mercury atmospheres, collection efficiencies of the popularly used media in the SASS train impinger assembly were investigated. This experimental work indicated that the 10% hydrogen peroxide and 0.2M ammonium persulfate solutions were only efficient up to 20 and 27%, respectively, for mercury collection from the generated test atmospheres. Both 0.2M ammonium persulfate with 0.025M silver nitrate and 1.5% acidified permanganate solutions showed better than 99% mercury collection efficiency. Sample storage stability and field use tests appear to be the next steps in validating the acidified medium as being acceptable for use in the SASS train system.

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Sampling	Stationary Sources	14B
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Mercury	SASS Train	07B
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ABSTRACT

A simple mercury vapor generator system based upon saturation of air with mercury vapor at a fixed temperature was assembled. Performance evaluation studies of the system indicated that stable atmospheres of mercury could be generated with control of the equilibration temperatures using Graham condensers. By adjusting the nitrogen flows over the mercury source reservoir and/or through a dilution flask, variable but known and stable mercury concentrations were generated and concurrently measured on a continuous basis with an on-line atomic absorption spectrometer (AAS). Through repeated sampling and analysis of the generated atmospheres and also calibration of the AAS, the absorbance readings for the AAS could be directly converted into mercury concentration, i.e., $\mu g/m^3$.

With stable and known mercury atmospheres, collection efficiencies of the popularly used media in the SASS train impinger assembly were investigated. This experimental work using a three-impinger assembly, SASS system and sampling rates between 3-6 cfm indicated that the 10 percent hydrogen peroxide and 0.2M ammonium persulfate solutions were only efficient up to 20 percent and 27 percent, respectively, for mercury collection from the generated test atmospheres. The 20 percent collection efficiency of the hydrogen peroxide impingers must be considered as a significant finding particularly because during SASS or EPA Method 5 sampling such oxidative impingers are generally ahead of impingers specifically used for mercury collection. The results of our study show that hydrogen peroxide impingers need to be also analyzed to obtain accurate and total mercury concentration in the flue gas. Both 0.2M ammonium persulfate with 0.025M silver nitrate and 1.5 percent acidified permanganate solutions showed better than 99 percent mercury collection efficiency. However, the former medium needs to be prepared freshly as aging of this solution for 48 hours has been found to decrease the collection efficiency to about 80 percent using a three-impinger sampling system.

The acidified potassium permanganate solution has been found to be generally satisfactory in terms of collection efficiency, ease of handling, and analytical quantification of samples. Thus, this medium should be subjected to sample storage stability and field use tests as the next steps in its validation as an acceptable medium for use in the SASS train system.

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SECTION 1.0
EXECUTIVE SUMMARY

1.1 SCOPE OF WORK

The objectives of this project work were to generate mercury atmospheres of known and stable concentrations and to evaluate collection efficiency of these atmospheres in three trapping media, namely 10 percent hydrogen peroxide, 0.2M ammonium persulfate and a mixture of 0.2M ammonium persulfate and 0.025M silver nitrate. A fourth medium, 1.5 percent potassium permanganate in 10 percent sulfuric acid, was added to the list during the course of the study.

1.2 MERCURY GENERATOR

A mercury vapor generating system capable of providing stable and known mercury atmospheres was designed and constructed and found to work satisfactorily. The generator consisted of a small enclosed vessel approximately 50 mL in capacity containing a pool of mercury (approximately 30-50 grams), followed by two Graham condensers in series with continuously circulating water at 2 $\pm$0.1°C and finally a 1000 mL capacity round bottom flask for diluting generated mercury levels to desired concentrations. Operation of the system was based on production of a precisely controlled, mercury-saturated atmosphere. Nitrogen gas at room temperature (20°C) was passed over the mercury pool and mercury, with its relatively high vapor pressure, vaporized into the nitrogen. The nitrogen was then passed through the two condensers at 2°C and a portion of the mercury condensed onto the condenser walls leaving a saturated atmosphere. The resulting mercury-saturated nitrogen stream was further diluted by means of the dilution flask to produce desired levels of mercury atmospheres.

The initial experimental work with the generator indicated that the maintenance of a precise cold temperature (2 $\pm$ 0.1°C) at the condensers was essential for stable generation. The stability of generated atmospheres was verified by directly feeding the air stream containing mercury from the dilution flask into a quartz cell placed in the light path of an atomic ab-

sorption spectrometer. The stability of mercury generation in terms of absorbance readings from the atomic absorption spectrometer was continuously monitored up to 5 hours using this in-situ analysis approach.

The AAS system used for the stability measurement was calibrated so that concentrations of mercury in the test atmosphere could be determined directly. To do this, a series of mercury standards in acidified $KMnO_4$ medium were prepared. Aliquots of these solutions were then treated with a reducing agent and the resulting elemental mercury vapor was passed through the quartz cell giving rise to peak-shaped signals. Next, mercury-containing test atmospheres were passed through $KMnO_4$ traps for known periods of time. The mercury samples thus collected were analyzed as per the standards. Assuming 100 percent collection efficiency for the $KMnO_4$ trap (see below) and comparing the calibration and collected sample analytical data, test atmosphere concentrations were calculated and plotted versus AAS readings.

1.3 EVALUATION OF MERCURY TRAPPING MEDIA

Evaluation of collection efficiency of media in a SASS sampling system involved sampling at the rate of 4 cfm. A second dilution of the mercury-containing stream was performed in a second 1000 mL round bottom flask using compressed air to provide the desired sample volume for sampling at this rate. During sampling with the SASS train impingers, the gas phase mercury concentrations at the inlet and at the outlet of the impinger system were monitored alternately with the atomic absorption spectrometer. To achieve this the quartz cell of AAS was connected to a small independent sampling pump to draw the test atmosphere containing mercury through the cell at a fixed rate of 1 L/min. Simple arrangement of two three-way valves enabled one to draw a sample from the nitrogen stream after the first dilution stage, from the air stream at the inlet of the impinger system, or from the air stream at the outlet of the impinger system. (See Figure 4.1). The collection efficiency of the medium could thus be monitored in real time while actual sampling was being carried out.

In all collection efficiency evaluation experiments, the generator system was started by adjusting the nitrogen flow over the mercury pool. Steady state generation was reached within 15 minutes as indicated by

stable absorbance readings on the AAS. To obtain background mercury readings due to compressed air and collection media solutions, sampling by SASS impingers was first started with only compressed air going into the second dilution stage. Steady state absorbance readings were monitored with the AAS both at the inlet and outlet of the impingers giving background or blank readings. After this the nitrogen stream containing mercury (from the first dilution stage) was allowed to go into the second dilution stage and sampling by impingers was performed to determine mercury collection efficiencies. The AAS was used to monitor the mercury concentrations in the air stream at the inlet and at the outlet of the impinger system. These readings provided real time evaluation of collection efficiencies by the media. Also, repeatability of readings at the inlet of the impingers indicated stability of the generation system. For all collection efficiency experiments, three SASS impingers were used and sampling was carried out typically for one hour. In all experiments the stability of generation was found to be excellent.

Collection efficiencies in four media were investigated. For such experimental work, three SASS train impingers in series were used, sampling rate was in the range of 3-5 cfm, sampling times were 30-60 minutes and low (10 $\mu g/m^3$) and high (100 $\mu g/m^3$) mercury concentrations in the air stream were used. The mercury collection media investigated included: 1) 10 percent hydrogen peroxide, 2) 0.2M ammonium persulfate, 3) freshly prepared and aged, 0.2M ammonium persulfate with 0.02M silver nitrate, and 4) 1.5 percent potassium permanganate in 10 percent sulfuric acid.

Of the four media studied, both 10 percent hydrogen peroxide and 0.2M ammonium persulfate showed poor mercury collection efficiency (<30 percent) and thus further investigation of these two media was discontinued. Both ammonium persulfate solution containing silver nitrate and acidified permanganate showed better than 99 percent collection efficiency at both low and high mercury concentrations in the test atmospheres. However, further studies with ammonium persulfate solution containing silver ions indicated that this solution needs to be prepared fresh, because a 48-hour old solution was found to collect only about 80 percent of the mercury. Acidified potassium permanganate was found to be a potentially satisfactory mercury collection medium because of the following:

- o Better than 99 percent collection efficiency in a two impinger sampling system
- o No aging effects on collection efficiency
- o Ease in handling permanganate solution
- o Analytical quantification of collected mercury in the samples is simple and reliable.

Because of these characteristics, it is recommended that the collection efficiency of this medium be further evaluated through field testing. Also, stability of mercury collected in the permanganate should be investigated before permanganate is recommended as the medium of choice for use in the SASS impinger system.

SECTION 2.0
INTRODUCTION

2.1 BACKGROUND

The stack emissions of trace elements during fossil fuel combustion in utility boilers has been of environmental concern for some time (2.1). Several investigators (2.2-2.4) have studied partitioning of various trace elements within the coal-fired power plants and some reports include measurement of size-dependent (2.5-2.7) trace element emissions from particulate control devices and investigation (2.8, 2.9) of mechanisms whereby respirable particles become enriched in volatile elements such as As, Sb, Se, Hg, etc. Depending upon boiler combustion conditions, these volatile trace elements are also emitted from utility stacks as vapors (2.2). It is the emissions of volatile trace elements as fine particles and/or vapors that are of environmental concern (2.10), particularly because these trace elements show toxicity potentials (2.11).

One chemical generally found in the emissions from fossil fuel combustion is mercury. The release of mercury vapor during combustion is a well recognized fact with estimates of the fraction of the feed coal mercury discharges ranging from 90 to 97 percent (2.12, 2.13). It is also reported that approximately 35 percent of the global atmospheric emissions of mercury from man's activities results from coal combustion (2.14). For a 1-ppm level of mercury in coal, its combustion in the utility boiler would result in stack emissions of 950 tons per year as popularly used particulate control devices do not show high collection efficiency for mercury (2.1). For purposes of monitoring and development of control technology, it is important that accurate and precise methods for sampling and analysis of source emissions of mercury be available. The primary focus of this project has been the evaluation of such sampling methods.

Commonly used sampling methods for determination of mercury emissions from stationary sources include the use of the Source Assessment Sampling System (SASS) or the EPA Method 5 train or similar sampling devices. In all these mercury collection devices, impingers containing chemical solutions

effective in collecting and retaining mercury and other volatile trace elements are used. For example, mercury vapors are collected in impinger(s) which contain oxidizing medium specifically used for the collection of this element. A literature search indicates investigators in the field have used a variety of chemical solutions with the view of optimizing the mercury collection efficiency. Such attempts were based on reports (2.12-2.15) which indicated lack of good mercury material balances during coal combustion because of use of inefficient mercury collection media. Some of the popularly used mercury collection substrates are listed below:

Mercury Collection into a Liquid

Potassium permanganate in sulfuric acid
Potassium permanganate in nitric acid
Iodine monochloride
Iodine/potassium iodide
Bromine, hypobromine
Carbonate-phosphate
Ethyl alcohol
99% isopropyl alcohol
Sodium borohydride
Acidic potassium dichromate
Acidic hydrogen peroxide
Ammonium persulfate
Silver-catalyzed ammonium persulfate
Hydrogen peroxide in ammonium hydroxide
Acidic hydrogen peroxide with silver nitrate
Nitric acid

Mercury Collection by a Solid

Activated carbon/charcoal
Activated carbon/charcoal treated with acid or base
Activated charcoal/mineral wool impregnated with:

iodine
ferric chloride
palladium chloride
cadmium sulfide

Silica gel or alumina coated with gold chloride

Hopcalite

Paper impregnated with:
potassium iodide
copper iodide
selenium
selenium sulfide

Mercury Amalgamation on a Metal Surface

Silver-gauze, wool, wire, thin-films, silvered Chromosorb P

Gold-foil, wire, chips, thin film

Platinum

Palladium

Copper

Zinc

Cadmium

Tin

Lead

Bismuth

In spite of a number of available media consisting of metals, sorbants and absorbing solutions, poor mercury collection efficiencies have been reported during stationary source sampling. This inefficiency probably contributed to the poor mercury mass balance achieved in a study of a coal-fired power plant (2.16-2.17). The cause(s) of inefficiency during flue gas sampling are not known but any combination of the following may be contributing factor(s): (2.18).

- o High sampling rate through the mercury collecting substrate which does not provide sufficient time for reaction changes to occur, i.e., reaction kinetics.

- o Flue gas contains chemical components which render the mercury collecting medium ineffective.
- o Flue gas contains mercury compounds other than those for which optimum substrate collection efficiency was evaluated in the laboratory.

2.2 PROJECT WORK BASIS

From this discussion it is clear that poor mercury collection efficiency during high volume sampling of flue gas has been of concern for sometime now and that investigators have focused on identifying collection media resulting in optimum collection efficiency. In general media selection considerations have been reagent purity, possible interferences during mercury quantification, collection efficiency for high volume sampling, reagent stability, cost and compatibility with other impingers in the sampling train assembly. A parameter given less attention has been the methodology for testing these various media. The analytical accuracy of "standard" sources of elemental mercury vapor used in past studies is questionable. Subsequently, the work to be described here was undertaken to (1) develop an accurate standard source of mercury vapor and (2) to test several of the more popular mercury collection media using this source. The basis of these efforts is that collection tests performed with a well-known vapor source would be more reliable than previous tests.

2.3 PROJECT OBJECTIVES

The objectives of the project were to generate known and stable atmospheres of mercury varying in concentrations, and to evaluate at the SASS sampling rate, mercury collection efficiency of the following media:

- o 10 percent hydrogen peroxide
- o 0.2M ammonium persulfate
- o 0.2M ammonium persulfate + 0.025M silver nitrate, freshly prepared and aged.
- o 1.5 percent potassium permanganate in 10 percent sulfuric acid.

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SECTION 3.0
EXPERIMENTAL

3.1 PRINCIPAL FOR THE MERCURY GENERATOR

The generation of stable and known concentrations of mercury in air is an important step for the evaluation of the collection efficiency of any medium. Because the vapor pressure of mercury is well known and relatively high, saturation techniques can be used for the generation of accurately defined test atmospheres. In the past Nelson (3.1) and Scheide, et. al. (3.2) have used this physical basis to generate known and stable atmospheres of mercury. Scheide, et. al., (3.3) performed some modifications to the earlier used generator system and have investigated various parameters that affect the performance of the generating system. Recently, Mercer (3.4) successfully used this type of generator to evaluate the mercury adsorptive capability of gold and silver surfaces.

The saturation method of generating test atmospheres of mercury involves introducing high levels of mercury vapor into a gas stream at an elevated temperature from a vaporizer/reservoir and then passing this stream through a condenser system at a lower temperature. Lowering the temperature results in saturation of the gas stream and excess mercury condenses out. To achieve saturation levels of mercury at the condenser temperature, it is necessary to evaporate an amount of mercury at the vaporizer/reservoir in excess of that required to achieve saturation levels at the lower condensation temperature. This can be achieved by maintaining the vaporizer/reservoir temperature sufficiently higher than the condensation temperature. An efficient gas-liquid contacting system is also required at the vaporizer/reservoir source to facilitate mercury mass transfer. Similarly, a sufficiently low gas flow rate through the vaporizer/reservoir is necessary to assure eventual saturation of the air stream in the condenser. The saturation level, i.e., concentration in the gas stream, can be very reproducible if the condenser temperature and stream flow rates are maintained precisely. The resulting saturated gas stream can be further diluted with additional

gas to produce the desired mercury concentration levels. Thus, by controlling the two gas flow rates and the temperature at the condenser, a wide range of mercury concentration levels can be generated.

3.2 MERCURY ATMOSPHERE GENERATION

Figure 3.1 shows the design and assembly of the mercury generator. It is essentially based on the design reported by Scheide, et. al., (3.3) with some modifications. A stream of carrier gas, nitrogen, is passed through a dryer and a 60 micron filter to remove impurities. Nitrogen was used as a carrier gas because it is available in a pure state and also to avoid oxidation of mercury. The nitrogen stream then passes through a flow meter and a regulating valve before it is split into two streams. One stream goes through a regulating valve and a high flow rotameter and then to the dilution flask. This stream is subsequently used for diluting the generated mercury levels to desired concentrations. The other nitrogen stream flows through a regulating valve, through a low flow rotameter and into the generator. The generator consists of: 1) A vaporizer/reservoir which is a small, enclosed 50 mL capacity flask (see Figure 3.2) electrically heated and temperature-controlled. (The flask contains 30-50 grams of mercury); 2) Two condensers, through which cold water (2°C) is continuously circulated. The temperature of the exit gas containing mercury is monitored by placing a thermometer on the top of the second condenser. The temperature of the condensers essentially determines the concentration of mercury in the nitrogen stream and thus precise temperature control at this stage is essential. Both condensers are wrapped with insulating material to minimize temperature changes and are connected to a small round bottom flask which collects condensed mercury. The temperature of the condensers is controlled to at least $\pm$ 0.1°C by connecting them to a water source from a bath capable of maintaining temperatures down to -5°C; 3) After leaving the condensers the gas stream containing mercury passes through a 1000 mL capacity round bottom dilution flask. In the flask the stream is diluted to produce the desired levels of airborne mercury. Then the diluted gas stream is fed into a quartz cell placed in an atomic absorption spectrometer (AAS) for direct mercury concentration measurement. The exhaust gases from the quartz cell

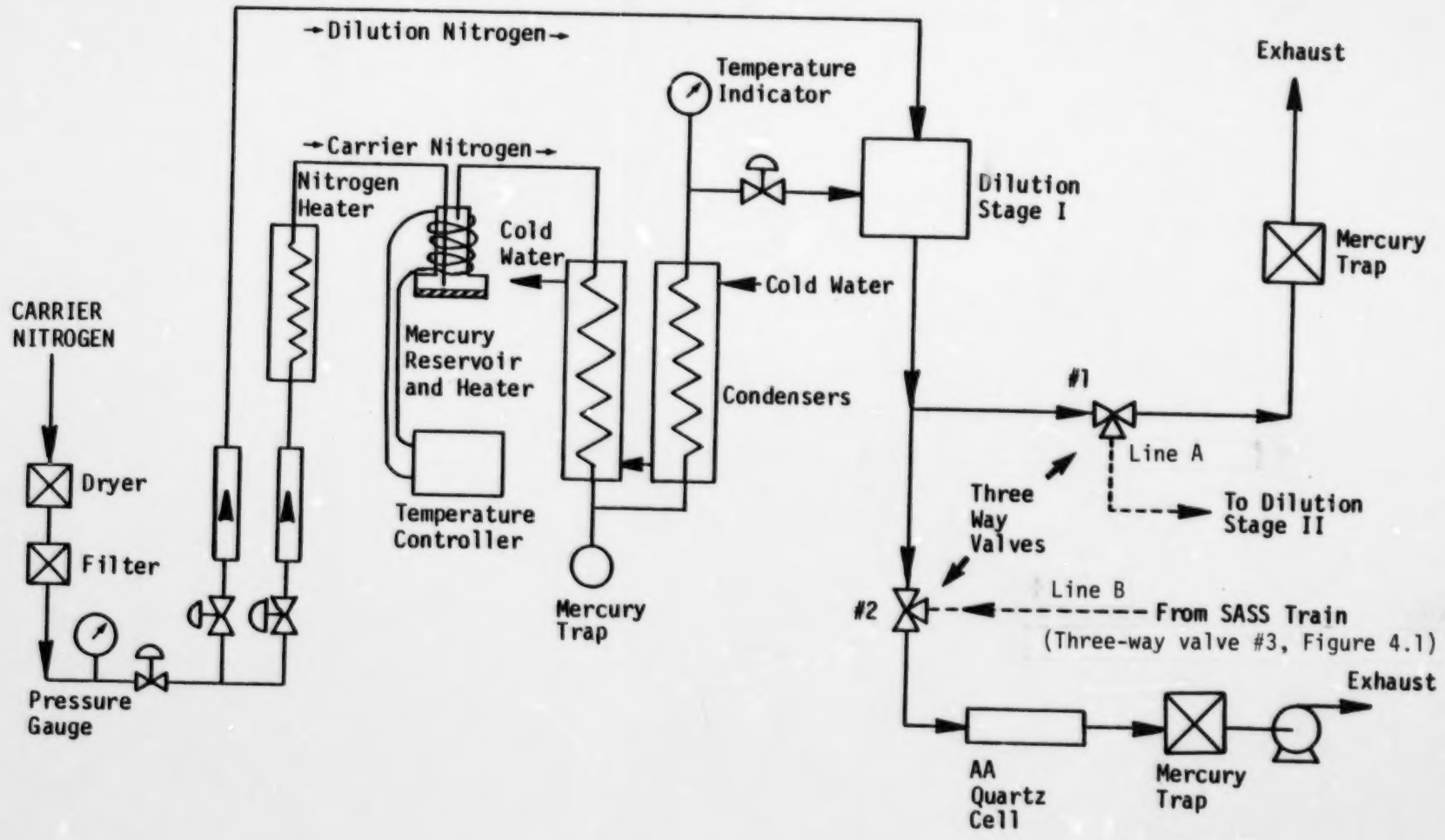


Figure 3.1: Schematic of Mercury Generation System

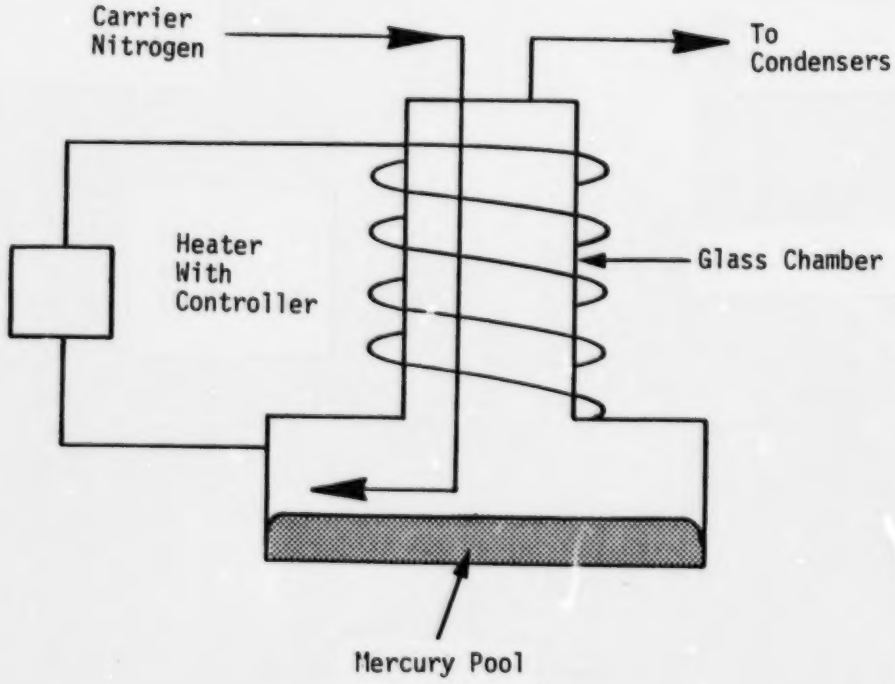


Figure 3.2. Mercury Vaporizer/Carrier

are fed into a mercury trap consisting of a mixture of activated charcoal and Hopcalite.

3.2.1 Generator Performance Evaluation

Initial experimental work with the generator included evaluation of its capability to produce stable atmospheres of mercury. For this experimental work the output from the dilution flask was passed directly through the quartz cell placed in the light path of the atomic absorption spectrometer (AAS), which provided readings in absorbance units. These absorbance readings were monitored as a measure of the stability of the mercury atmosphere generation.

On the basis of a published report, (3.3), mercury vapor generation was initially started by maintaining the mercury reservoir temperature at 60°C and the condensers' temperature at 2°C. Nitrogen as a carrier gas was passed through the mercury reservoir at a steady rate of 1.7 L/min. Nitrogen was also used to dilute the mercury test atmospheres to desired concentration ranges. The flow through the dilution flask was 7.3 L/min. The output from the dilution flask was passed through the quartz cell to record absorbance. With these generation conditions, it was observed that stable mercury generation was not possible as absorbance readings were not stable. Further experimental work with the generator system indicated that increasing or decreasing the reservoir temperature over a range of 22 to 60°C did not affect generation stability and that the required mercury concentration in the test atmospheres could be generated without application of heat to the mercury reservoir. It was also experimentally established that circulation of cold water at a precise temperature of 2 ± 0.1°C through the condensers was essential to the generation of stable levels of mercury.

Thus, for stable mercury vapor generation, the following were determined:

- It is not necessary to heat the mercury reservoir for generation of mercury atmospheres in the range of 10 to 100 $\mu g/m^3$, which is the estimated range of source emissions.
- Mercury vapors of desired concentration range can be generated with the vaporizer/reservoir at room temperature and a slight variation of the reservoir temperture has very little effect on the stability of generation.

- o Maintenance of a precise (±0.1°C) low temperature of 2°C at the condensers is found to be essential for stable mercury atmosphere generation.

- o A steady (±5%), low flow of the nitrogen through the mercury reservoir is required (range 0.25 to 1.85 L/min) for the desired mercury concentration ranges.

- o A steady flow of nitrogen is found to be essential for the dilution of generated mercury atmospheres. Dilution ratios in the range of 4.95 to 26.2 could be used for mercury generation. Higher or lower levels of mercury atmospheres could be generated by changing dilution ratios and flow through the mercury reservoir.

Using the above conditions, test mercury atmospheres were generated and the outlet stream from the dilution flask was passed through the quartz cell placed in the light path of the atomic absorption spectrometer (AAS). The AAS provided a direct indication of steady generation of mercury vapor in terms of steady absorbance readings which were monitored on a strip chart recorder. Typical absorbance data obtained are tabulated in Table 3.1 and Figure 3.3 shows the steady generation of mercury for more than a five hour period as monitored using a strip chart recorder.

3.2.1.1 Mercury Generation - Sampling--

After having optimized the generation system, the next step was to determine the concentrations of mercury in the test atmospheres. For this, the system connections and tubing after the dilution flask were modified slightly. The modifications included incorporation of two three-way valves, one after the dilution flask and one before the quartz absorption cell. With these changes the test atmosphere containing mercury could be passed directly through the quartz cell, or when required for concentration determinations (i.e., calibration) or collection efficiency evaluations, could be passed through the impingers. The gas exiting from the last impinger was permitted to go to the quartz cell via a moisture trap containing magnesium perchlorate and second three-way valve. The exhaust from the quartz cell was passed through a trap that contained a mixture of activated charcoal and Hopcalite. A pump to pull the test gas and a flow meter to measure the flow of the gas through the impingers and the mercury trap were incorporated. These system modifications were intended to provide:

TABLE 3.1

PRECISION OF MERCURY GENERATION

Date	Time	Absorbance
Aug. 6 '82	10:10 a.m.	0.246
	10:35 a.m.	0.235
	11:25 a.m.	0.227
	11:46 a.m.	0.226
	11:55 a.m.	0.224
	12:07 p.m.	0.224
	12:20 p.m.	0.223
Aug. 11 '82	10:08 a.m.	0.415 (Generation began)
	10:18 a.m.	0.214
	10:36 a.m.	0.210
	10:57 a.m.	0.202
	11:37 a.m.	0.198
	11:40 a.m.	0.206
	12:14 a.m.	0.206
	12:37 a.m.	0.207
	1:05 p.m.	0.207
	1:35 p.m.	0.207
	2:35 p.m.	0.222

Temperature around the mercury reservoir was 15°C.
Nitrogen flow through the reservoir was 1.1 L/min and through the dilution flask was 7.3 L/min. Dilution ratio was 7.7.

Figure 3.3. Absorbance vs. time plot showing stability of mercury vapor generator.

- o Quantitative determinations of the generated mercury concentrations in the test atmospheres via sampling.
- o Assessment of collection efficiencies of the mercury trapping media while sampling is being carried out.
- o Development of an experimental relationship between mercury concentrations (obtained by analyzing collected samples) and absorbance readings on the AAS.

The mercury vapor concentrations in the test atmospheres were experimentally determined by collecting vapor for a known period of time in two impingers in series and then analyzing the impinger solutions. The collection medium was 1.5 percent potassium permanganate in 10 percent (v/v) sulfuric acid; 50 ml of this medium was contained in each impinger which were of 75 mL capacity. The exit gas from the second impinger was fed into the quartz absorption cell.

Before sampling began, the generator was started and a steady generation state was established (1 to 15 min) as evidenced by steady AAS absorbance readings and strip chart recordings. Then the sampling was begun by turning the three-way valve so that the mercury test atmospheres passed through the two impingers and then through the quartz AAS cell. After sampling was completed (anywhere from 15 min to 40 min), the three-way valve was switched back to a position which permitted the test atmosphere to pass directly through the quartz cell to further verify the precision of the generation.

Replicate samples were collected to evaluate the precision of generation and sampling. In all instances during actual sampling, the AAS absorbance readings were almost zero indicating essentially 100 percent collection efficiency of the $KMnO_4/H_2SO_4$ medium. Similarly, the stability of generation was observed to be excellent; that is, the AAS absorbance readings were essentially the same before and after each sample collection. The stability of generation and sampling precision were also verified by collecting two samples simultaneously. The mercury concentrations determined (See Section 3.2.1.2) in the two samples were 0.34 µg/L. and 0.38 µg/L., respectively. Sampling time for sample No. 1 was 40 minutes and sample No. 2, 30 minutes. Sampling rates in both cases was 0.98 L/min and two

impingers in series, each containing 50 mL of 1.5 percent $KMnO_4$ in 10 percent H_2SO_4, were used.

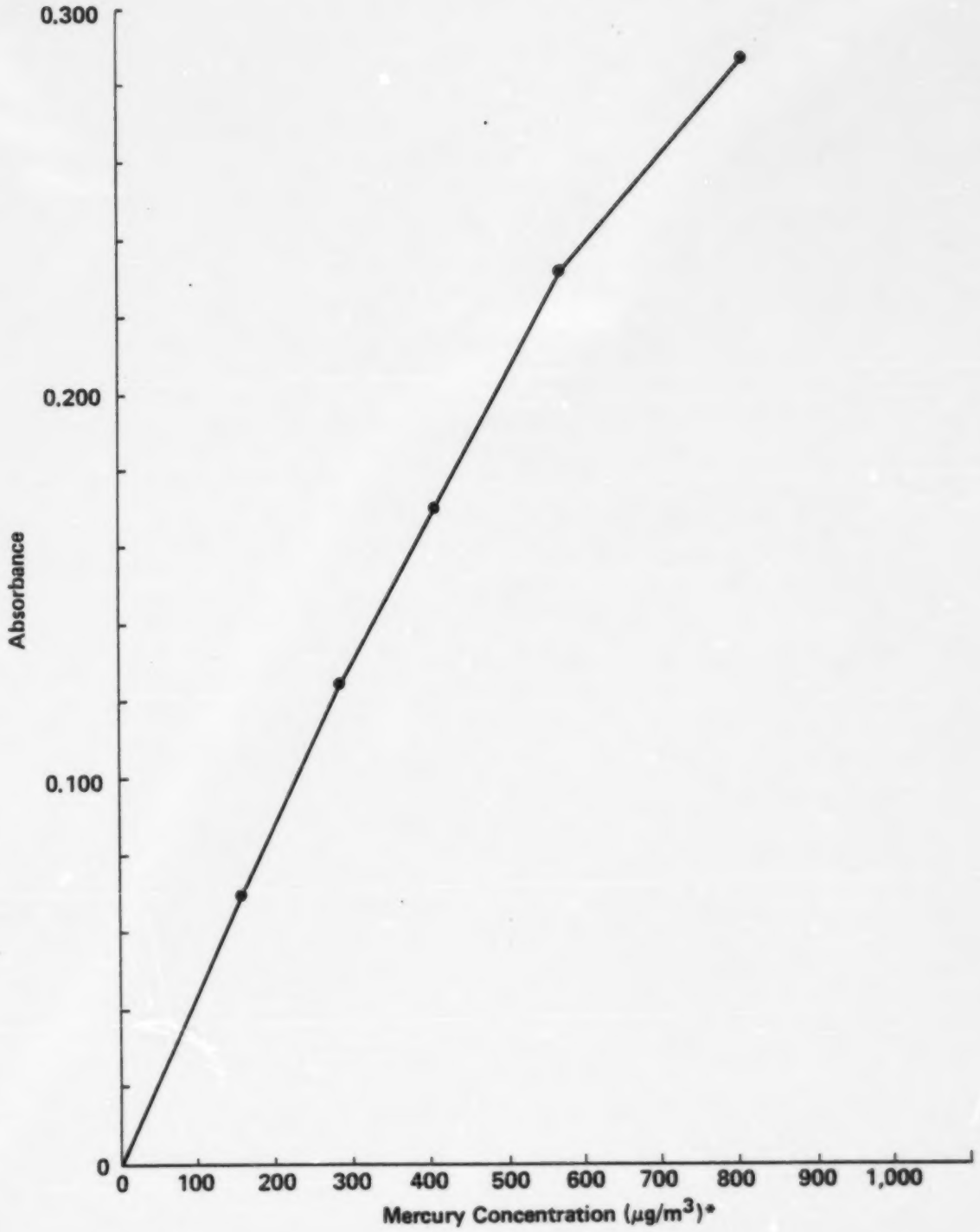
Further experimental work included generation of test atmospheres that contained varying levels of mercury. This was achieved by increasing or decreasing the dilution ratio. Rapid change in the mercury concentrations was monitored via changes in the AAS absorbance readings. Further, samples were collected to establish a relationship between experimentally determined mercury concentrations in the test atmospheres and absorbance. For this, the dilution ratio was set and steady absorbance was achieved. Then samples were collected and analyzed. Next absorbance was changed to another desired level (eg., from 0.070 to 0.287 units) by adjusting the dilution ratio, steady state was monitored on the strip chart recorder, and samples were collected and analyzed to determine mercury levels. Figure 3.4 shows that a linear relationship exists between experimentally determined mercury concentrations and AAS absorbance. Consideration of data in Figure 3.4 indicates that AAS absorbance could be set and changed and that monitored absorbance was directly proportional to mercury concentrations in the generated test atmospheres. For such absorbance reading changes, flow through the mercury reservoir and/or dilution flask could be changed. Therefore, further experimental work included optimizing the nitrogen gas flow through the mercury reservoir and dilution flask to obtain desired absorbance readings which were experimentally found to be proportional to mercury concentrations in the test atmospheres. Typical data obtained are tabulated in Table 3.2.

A summary of this experimental work indicates that:

- Known and stable mercury levels can be generated with the designed generator system
- Mercury concentrations of desired levels can be generated by adjusting dilution gas (nitrogen ratio).
- Observed AAS absorbance is proportional to generated mercury concentrations in the test atmospheres.

3.2.1.2 Sample Analysis Procedure--

All samples were analyzed for mercury by following the procedure (Ref. 3.5) that first involved reduction of excess $KMnO_4$ with hydroxylamine hydrochloride solution (1.5 percent w/v) and then dilution of the resulting



*Determined by collection into two impingers each containing 50 mL of 1.5% $KMnO_4$ in 10% H_2SO_4.

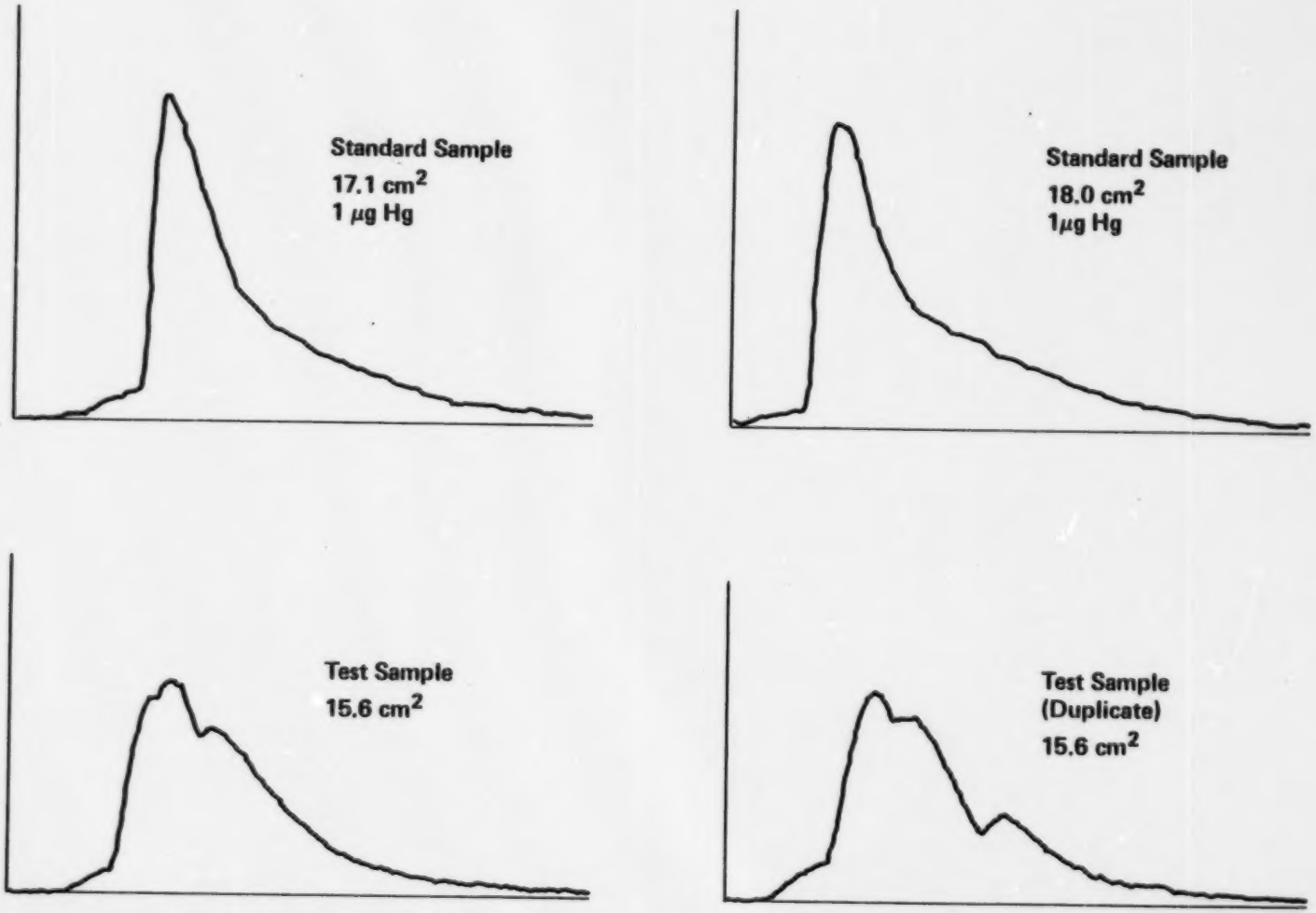
Figure 3.4. Absorbance vs. generated mercury concentration.

TABLE 3.2

OPTIMIZATION OF NITROGEN FLOW THROUGH MERCURY RESERVOIR AND DILUTION FLASK

Carrier N_2 Flow Rate L/min.	Dilution N_2 Flow Rate L/min.	Dilution Ratio	AAS Reading
0.29	7.31	26.2	0.079, 0.074
0.29	6.33	22.8	0.085
0.29	4.23	15.6	0.124, 0.125
0.29	2.04	8.03	0.235
0.51	7.31	15.33	0.119, 0.116
0.51	6.33	13.41	0.133
0.51	4.23	9.29	0.197
0.72	7.31	11.15	0.153
0.906	7.31	9.03	0.190
1.09	7.31	7.71	0.225, 0.222
1.85	7.31	4.95	0.338

solution to a known volume. An aliquot of this solution was transferred to a mercury reduction cell (Varian Model 65). Sodium borohydride was added, and the resulting elemental mercury was swept into the quartz cell placed in the light path of the AAS; the AAS signal was recorded on a strip chart recorder. The mercury concentrations of samples were determined using a calibration curve which was obtained by analyzing standard mercury solutions prepared with the 1.5 percent $KMnO_4$ in 10 percent H_2SO_4 matrix. Quantification was performed through comparison of absorption peak areas obtained with impinger and standard solutions. All samples from the second $KMnO_4$ impingers were found to contain mercury levels below the detection limits of the method which was 0.05 µg of mercury. Precisions of standard and sample analyses from the 1.5 percent $KMnO_4$ in 10 percent H_2SO_4 are shown in Figure 3.5. Precision for both samples and standard analyses was determined to be satisfactory and spiked sample recovery was better than 90 percent indicating no interferences from solution medium during analysis. A typical calibration curve using mercury standards in 1.5 percent $KMnO_4$ in 10 percent H_2SO_4 is shown in Figure 3.6.



NOTE: Collection media is 1.5% $KMnO_4$ in 10% H_2SO_4.

Figure 3.5. Precision of standard and test sample analyses.

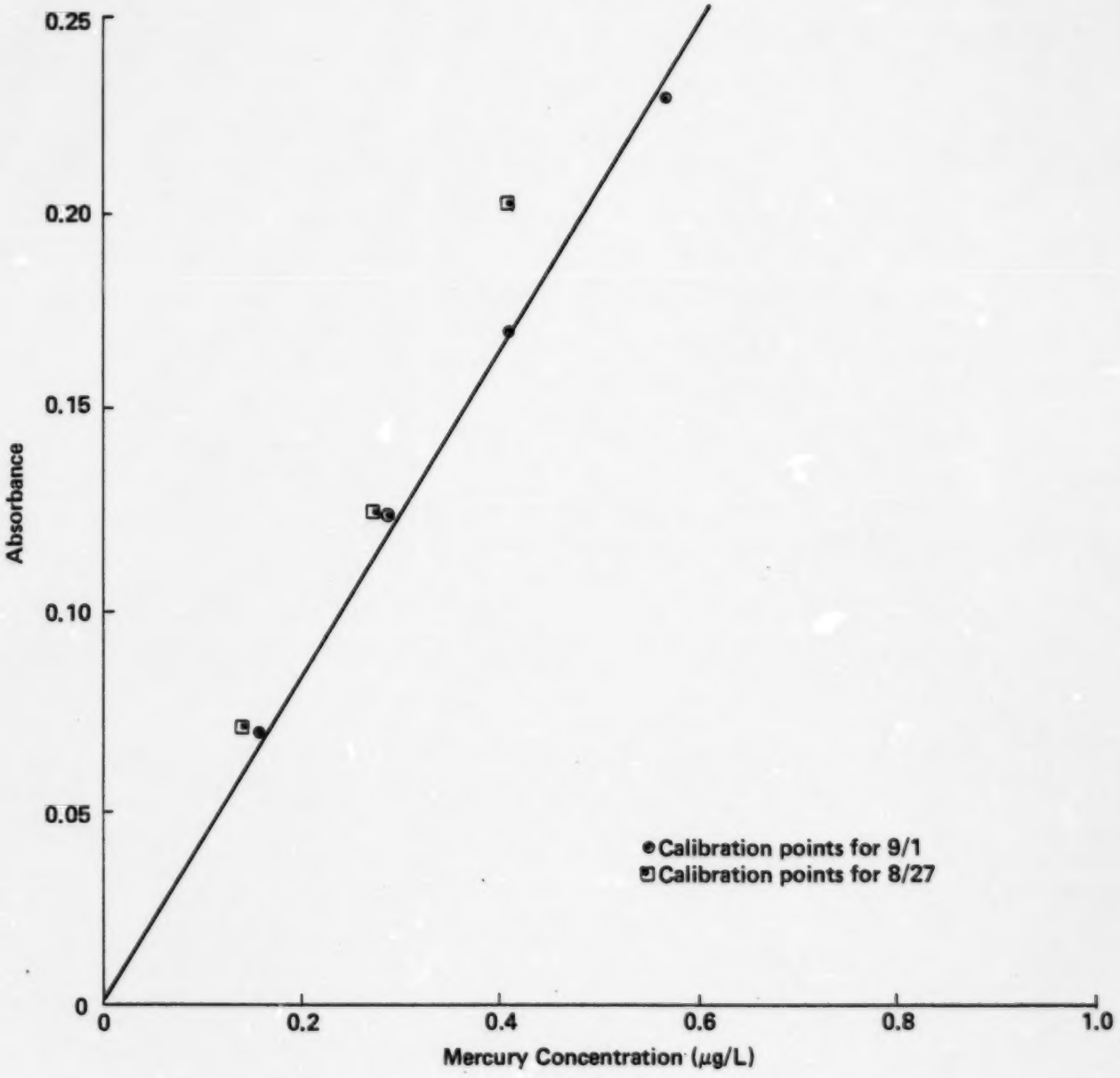


Figure 3.6. Calibration curves for mercury solution 1.5% in $KMnO_4$ and 10% in H_2SO_4.

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SECTION 4.0
EVALUATIONS OF MERCURY TRAPPING MEDIA AND RESULTS AND DISCUSSION

With the successful generation of known and stable mercury atmospheres evaluation of collection efficiency at high volume sampling rates became the objective of the project work. For this experimental work some changes were made and these included:

- Addition of a second 1000 mL dilution flask which followed the first dilution flask (See Figure 3.1) and through which filtered compressed air was passed at a high volume rate, 3-6 cfm.
- Use of three SASS train impingers in series replacing 75 mL impingers in the sampling system discussed earlier. (See Section 3). The commercially available SASS impingers had some metal parts which were replaced so that all parts of the sampling system including impingers were made of glass and/or Teflon. Such changes were considered essential to avoid losses of mercury, if any, due to amalgamation on metal surface.
- A high volume sampling pump was incorporated so that samples could be collected at the SASS sampling rate, i.e., 3-6 cfm. The pump used was calibrated using a wet test meter.
- Incorporation of one additional three-way valve after the second dilution flask so that mercury test atmospheres could be directly fed to the quartz absorption cell on the AAS or passed through the impingers and then into the quartz cell via a moisture trap. Dilution air alone passed through the second dilution flask and into the quartz cell permitted evaluation of the blank contribution to the absorbance signal. Additionally, stability of mercury generation could be monitored instantly during sampling for any interval of time. The quartz AAS cell was connected to an independent small pump which allowed drawing test atmosphere through the cell at a fixed rate of 1 L/min.

4.1 COLLECTION MEDIA

With the changes in the system for sampling at SASS sample collection rates made, the media listed below were tested for mercury collection efficiency:

1) 10 percent hydrogen peroxide (v/v)
2) 10 percent hydrogen peroxide in 10 percent sulfuric acid

3) 0.2M ammonium persulfate (w/v)
4) Freshly prepared solution of 0.2M ammonium persulfate + 0.025M silver nitrate (w/v).
5) Aged (48 hours) solution of 0.2M ammonium persulfate + 0.025M silver nitrate
6) 1.5 percent potassium permanganate in 10 percent sulfuric acid.

4.2 SAMPLING FOR COLLECTION EFFICIENCY EVALUATIONS

The sampling operation to evaluate mercury collection efficiency of a medium typically involved the following steps:

1) Start the circulation of cold water (2 $\pm$ 0.1°C) through the condensers and wait for the temperature to stablize at the condensers (3-5 minutes)

2) Turn on the atomic absorption spectrometer (AAS) and set the absorbance to zero. Then start the sampling pump that draws air through the quartz AAS cell.

3) Place 250 mL of solution of the mercury trapping medium under investigation in each of the three SASS impingers and make connections (secured tightly) so that impingers are connected in series for sampling.

4) Start the nitrogen gas flows through the mercury reservoir and the first dilution flask. Position the three-way valves in such a direction so that a portion of the outlet gas stream from the first dilution flask passes through the quartz AAS cell. Wait to achieve steady state (5-15 minutes) mercury generation as indicated by steady absorbance readings. Divert the outlet gas stream to an absolute trap containing a mixture of activated charcoal and Hopcalite after steady generation is achieved.

5) Start the high volume sampling pump and also the flow of compressed air through the second dilution flask Now switch the three-way valve so that a portion of the outlet air stream from the second dilution flask passes through the quartz AAS cell.

6) With the impinger high-volume pump on, switch the three-way valve to a position so that the outlet air stream from the third impinger is sampled by the quartz AAS cell. At this stage the air does not contain mercury vapor since the stream from the outlet of the first dilution flask is being diverted into an absolute trap with the use of a three-way valve. This step provides a measure of the blank contributions of the compressed air and impinger atmospheres to the AAS absorbance signal.

7) Now turn the three-way valve after the first dilution flask so that the nitrogen gas stream containing mercury enters the second dilution flask, is diluted with compressed air, and then goes through the impinger collection medium. Also note the time of start and

reading on the magnehelic guage. Draw samples through the quartz AAS cell alternately from the air stream at the inlet of the impingers and the outlet of the impingers. Note steady readings from both streams.

8) Sample for the desired length of time (one hour was sampling time in the experimental work) to evaluate collection efficiency of the medium. Also note constancy of readings for the air stream at the inlet of the impingers. This would indicate generator stability.

9) Repeat step no. 4 after sampling is over to determine that stability of mercury generation existed at completion of sampling.

The sampling system together with three-way valves, pumps, flow meter, etc., is shown is Figure 4.1 and Figure 4.2 depicts typical sampling and medium collection efficiency events as recorded on the strip chart recorder when using 1.5 percent $KMnO_4$ in 10 percent H_2SO_4. Sampling time was one hour and each of the three impingers had 250 mL of trapping medium.

Utilizing the mercury atmosphere generation system and the sampling approach described, the collection efficiencies of the popularly used media were investigated.

4.2.1 10 Percent Hydrogen Peroxide

Three SASS impingers in series each containing 250 mL of 10 percent hydrogen peroxide solution were used for collection efficiency evaluations. Three sampling runs were made at test atmosphere mercury concentrations of 70 $\mu g/m^3$ and one run was made at a mercury concentration of 10 $\mu g/m^3$. The data obtained are tabulated in Table 4.1. As noted in the table, the collection efficiency of the medium was poor, i.e., only about 20 percent. Further experiments at low mercury levels with acidification of the hydrogen peroxide with 10 percent sulfuric acid did not improve its collection efficiency, which remained about 20 percent.

The collection efficiency calculations are based only on the relative absorbance readings of the AAS taken at the inlet and outlet of the impingers. This method of calculating collection efficiency is considered valid (although not quantitative) in view of the fact that a linear relationship between AAS absorbance readings and mercury concentrations in the test atmospheres was established.

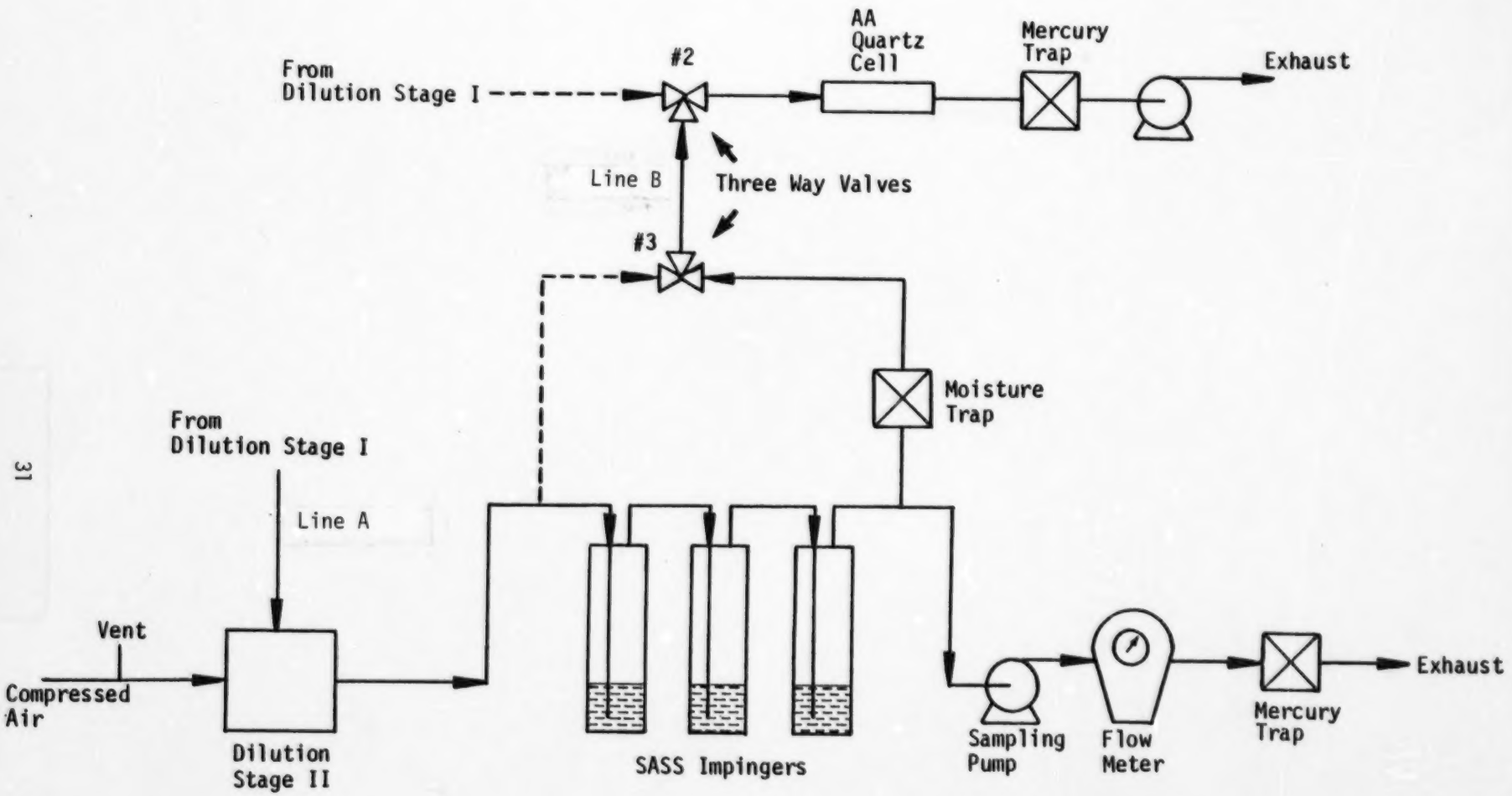

Figure 4.1: SASS Impinger Sampling System and Online AAS Monitoring System

Figure 4.2. Recording of absorbance vs. time at various points in the mercury vapor generation/sampling system.

TABLE 4.1

MERCURY COLLECTION EFFICIENCY IN 10% HYDROGEN PEROXIDE IMPINGERS[a]

Run No.	Sampling Rate (cfm)	Sampling Time	% Efficiency
1	4.10	60 min.	21.4
2	4.10	60 min.	19.0
3	4.21	60 min.	20.8
4[b]	3.93	60 min.	18.2
5[c]	4.62	60 min.	22.2
		Ave =	20.3

[a] Three impingers in series were used. Room temperature was 25°C.

[b] Three impingers used; each contained 250 mL of 10% hydrogen peroxide in 10% sulfuric acid.

[c] Mercury concentrations in the test atmospheres were about 10µg/m^3. The rest of the runs had mercury levels of 70µg/m^3.

During this effort, the procedure given in the EPA Level 1 Manual (4.1) was followed for analysis of the hydrogen peroxide medium. This involved taking a 10 mL aliquot of the hydrogen peroxide solution and adding 5 percent, acidified permanganate solution to destroy excess peroxide. Our experience indicates that one needs to add a considerable volume of permanganate solution to destroy the excess peroxide; this point should be emphasized in the Level 1 EPA Manual. Because of this and possible other reasons such as mercury losses during removal of excess hydrogen peroxide, the sample analysis data showed poor precision and accuracy. Further attempts to investigate this problem were discontinued mainly because of time and budgetary constraints. Storage stability of mercury ions in such a medium also needs to be investigated, particularly in light of a recent report (4.2) that indicates mercury ions are difficult to stabilize in solutions.

Although inefficient, the collection of about 20 percent of the mercury vapor by the hydrogen peroxide impingers must be considered significant in terms of mercury distribution in the SASS train impinger train. Generally, hydrogen peroxide impingers in the SASS train or EPA Method 5 train precede mercury collecting impingers. This project work indicates that these hydrogen peroxide impingers also need to be analyzed to get true concentrations of mercury emitted from a stationary source.

4.2.2 0.2M Ammonium Persulfate

The collection efficiency of this medium was evaluated both at low (10 $\mu g/m^3$) and high (70 $\mu g/m^3$) mercury levels in test atmospheres using three impingers in series; each impinger contained 250 mL of collection substrate. The collection efficiency at the high mercury concentration was 28* percent and at the low mercury concentration was 25* percent. Because of this poor collection efficiency, additional tests were not performed with this medium. Again impingers were not analyzed for mercury and collection efficiency calculations were based on inlet and outlet absorbances as monitored with the AAS and strip chart recorder. In both kinds of sampling (i.e., low and high mercury levels), sampling times were 60 minutes and sampling rate was 3.75 cfm.

*Estimated coefficient of variation is 10 percent.

4.2.3 0.2M Ammonium Persulfate with 0.025M Silver Nitrate

A 250 mL portion of freshly prepared solution of this medium was placed in each of the three impingers and collection efficiency was evaluated by sampling both at low and high mercury levels in the generated test atmospheres. Duplicate sampling runs at both mercury levels showed better than 99 percent collection efficiency with the three impinger SASS sampling system. The sampling time in all cases was 60 minutes and the sampling rate was close to 4 cfm. Again no attempt was made to determine mercury concentrations in the impingers and thus analytical data on the collection efficiency of the individual impingers are not available. However, a sampling run at the 70 $\mu g/m^3$ mercury level was conducted with only one impinger that contained a freshly prepared solution of 0.2M ammonium persulfate with 0.025M silver nitrate. The sampling rate was 4.33 cfm and sampling time 60 minutes. The collection efficiency of the one impinger based on inlet/outlet AAS absorbances was determined to be only 74* percent. This experimental work indicates that for better than 98 percent mercury collection efficiency, three SASS impingers each containing 250 mL of this medium are required.

Further collection efficiency evaluation work included aging of the 0.2M ammonium persulfate/0.025M silver nitrate solution for 48 hours in a refrigerator and then using it in the three impingers. The collection efficiency of the medium at high mercury concentration was found to have gone down to 82* percent and for low concentration was 79* percent. For both levels of mercury, the sampling time was 40 minutes, and the sampling rate was 3.75 cfm. Here too, impingers were not analyzed and efficiency calculations were based on the absorbances at the inlet and outlet of the impingers.

4.2.4 1.5 Percent Potassium Permanganate with 10 Percent Sulfuric Acid

This medium was used because of its reported (5.3) optimum collection efficiency of mercury in a flue gas source burning a high sulfur coal. Three SASS impingers each containing 250 mL of this medium at high (70 $\mu g/m^3$) and low (10 $\mu g/m^3$) mercury levels in test atmospheres were tested. For these experimental evaluations, sampling time was 60 minutes at

*Estimated coefficient of variation is 10 percent.

high mercury levels and the sampling rate was 4 cfm. At low mercury levels samples were collected only for 25 minutes and the rate was 4.34 cfm. In both instances the collection efficiency was found to be better than 99 percent with the three impinger sampling system. However, one impinger containing 250 mL of acidified potassium permanganate was found to collect 94* percent of mercury from the test atmospheres containing high levels of mercury. For such an evaluation, sampling rate was 5.24 cfm and time of collection was 60 minutes. This result indicates that for better than 99 percent mercury collection efficiency, two impingers each containing 250 mL of acidified potassium permanganate are adequate.

In all of this experimental work, collection efficiency calculations were based on absorbance readings at the inlet and outlet of the impingers. No attempts were made to analyze the impingers individually because of time and budgetary limitations, although a satisfactory analysis procedure for measurement of mercury in the acidified potassium permanganate matrix was established earlier (see Section 3 for details). This medium appears suitable for use in the SASS train impinger assembly because of its optimum collection efficiency, ease of handling and the availability of an analysis procedure.

Table 4.2 summarizes the collection efficiency of each of the media investigated.

*Estimated coefficient of variation is 10 percent.

TABLE 4.2

SUMMARY OF MERCURY COLLECTION EFFICIENCY OF VARIOUS MEDIA[a]

Medium	No of Runs	Average Sampling Rate (cfm)	Average Collection Efficiency
10% hydrogen peroxide	4[b]	4.25	20.9
Acidified 10% hydrogen peroxide	1	3.93	18.2
0.2M ammonium persulfate	2[b]	3.75	26.8
Freshly prepared 0.2M ammonium persulfate + 0.025M silver nitrate	4[c]	4.00	>99.0
Freshly prepared 0.2M ammonium persulfate + 0.025M silver nitrate	1[d]	4.33	73.3
Aged 0.2M ammonium persulfate + 0.025M silver nitrate[e]	2[b]	3.75	80.1
1.5 percent potassium permanganate in 10% sulfuric acid[f]	2[b]	4.67	>99.0
1.5 percent potassium permanganate in 10% sulfuric acid	1[d]	5.24	94.4

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a Three impinger system was used unless otherwise specified. Sampling times in most cases were 60 minutes; exceptions are mentioned in the text. Room temperature was in the range of 20-25°C and data on efficiency are based on relative absorbance readings at the inlet and outlet of the impingers.

b Includes one run at low mercury levels.

c Includes two runs at low mercury levels.

d Only one impinger containing 250 mL of medium was used.

e Aged for 48 hours in the refrigerator.

f Sampling times less than 60 minutes. See details in text.

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SECTION 5.0
CONCLUSIONS AND RECOMMENDATIONS

5.1 GENERAL CONCLUSIONS

- A mercury generator system was successfully designed and assembled.
- The system was found to generate stable and desired levels of mercury atmospheres.
- Maintenance of a low (2°C) and precise temperature at the condensers was determined to be extremely important for stable mercury concentration generation.
- By adjusting the nitrogen flows of the carrier gas through the mercury reservoir and through the dilution flask, desired levels of mercury could be generated.
- On-line incorporation of an atomic absorption spectrometer equipped with a quartz absorption cell provides an easy method for monitoring continuously the generated mercury concentrations.
- On-line incorporation of the atomic absorption spectrometer equipped with a mercury cell permits collection efficiency evaluations of media while samples are being collected.
- There is a direct and linear relationship between absorbance and nitrogen flow over the mercury pool and through the dilution flask.
- Atomic absorption absorbance readings were found to be linearly proportional to generated mercury concentrations.

5.2 COLLECTION MEDIA TEST RESULTS

- Three impingers, each containing 250 mL of 10 percent hydrogen peroxide solution were found to collect only up to 20 percent of the mercury from the test atmospheres. Acidification of 10 percent hydrogen peroxide solution with 10 percent sulfuric acid did not improve collection efficiency.
- Three impingers each containing freshly prepared 250 mL of 0.2M ammonium persulfate solution and 0.02M silver nitrate showed better than 99 percent mercury collection efficiency with low (10 $\mu g/m^3$) and high (70 $\mu g/m^3$) mercury test atmospheres. However, use of one impinger brought down the collection efficiency to about 73 percent. Therefore, for better than 99 percent collection efficiency, three impingers need to be used.

- o Aging of the ammonium persulfate solution containing silver nitrate affects the collection efficiency and a 48-hour old solution was found to collect only up to 80 percent of the mercury using three impingers.

- o Three impingers each containing 250 mL of 2 percent potassium permanganate in 10 percent sulfuric acid were found to yield better than 99 percent collection efficiency with both low (10 $\mu g/m^3$) and high (70 $\mu g/m^3$) mercury concentrations in the airstream. One acidified permanganate impinger was found to collect over 94 percent of the mercury from a test atmosphere that contained mercury levels of 70 $\mu g/m^3$. Thus, a two SASS impinger sampling assembly should be sufficient for optimum mercury collection efficiency.

5.3 RECOMMENDATIONS

The collection efficiency of the 1.5 percent acidified potassium permanganate solution needs to be verified for mercury contained in the flue gas originating from fossil fuel combustion. Similarly, collection efficiency needs to be verified by performing material balance, i.e., by analyzing individual impinger solutions. Although acidified potassium permanganate appears to be an efficient medium for mercury collection, it has stability and storage problems and these need to be investigated further. Other efficient mercury collection media also need to be explored. Collection substrates such as iodized charcoal, Hopcalite, iodine monochloride, and acidified potassium dichromate are a few of our recommendations. Additionally, filter paper impregnated with a medium needs to be evaluated for mercury collection efficiency, ease of field handling, stability during sample storage and any analytical quantification problems.

During this project work it was found that 10 percent hydrogen peroxide solution with or without acidification collected up to 20 percent of the mercury. This observation must be considered significant in terms of mercury distribution in the SASS train impinger system. Generally, hydrogen peroxide impingers in the SASS train or EPA Method 5 train are ahead of mercury collecting impingers. This project work indicates that hydrogen peroxide impingers should be also analyzed for mercury after flue gas sampling. Storage stability of collected mercury samples in such a medium needs to considered as recent work by Shendrikar and Filby (5) indicates serious mercury losses onto the storage container walls during 100 days of storage. The analytical quantification problem from the hydrogen peroxide matrix

needs to be explored. During this project work, the procedure given in the EPA Level 1 Manual (5.2) was followed to destroy excess hydrogen peroxide after sampling. Our experience indicates one needs to add a considerable volume of 5 percent potassium permanganate solution to remove excess hydrogen peroxide from the samples. This point needs to be clearly mentioned in the procedure included in the Level 1 manual. The EPA Level 1 manual also includes a procedure for analyzing mercury samples from ammonium persulfate solution containing silver ions. The losses of mercury during silver precipitation as silver chloride needs to be addressed fully. Such an investigation may be carried out using Hg^{203} radiotracer to increase percent confidence in the data.

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